

10/511290

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
30 October 2003 (30.10.2003)

PCT

(10) International Publication Number
WO 03/089675 A1(51) International Patent Classification⁷: **C22B 3/42 //**
15:00SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/FI03/00292

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(22) International Filing Date: 15 April 2003 (15.04.2003)

(25) Filing Language: Finnish

(26) Publication Language: English

(30) Priority Data:
20020749 19 April 2002 (19.04.2002) FI(71) Applicant (*for all designated States except US*): **OUTOKUMPU OYJ** [FI/FI]; Riihitontuntie 7, FIN-02200 Espoo (FI).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **LEIMALA, Raimo** [FI/FI]; Harjutie 30, FIN-28430 Pori (FI).(74) Agent: **OUTOKUMPU OYJ**; Intellectual Property Management, P.O. Box 27, FIN-02201 Espoo (FI).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
- *of inventorship (Rule 4.17(iv)) for US only*

Published:

- *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR THE PURIFICATION OF COPPER CHLORIDE SOLUTION

(57) Abstract: The invention relates to a method for the removal of metal impurities in chloride-based copper recovery processes. The amount of impurities in a strong chloride solution of monovalent copper can be reduced according to the method down to very low levels by using ion exchange as at least one purification stage.

WO 03/089675 A1

METHOD FOR THE PURIFICATION OF COPPER CHLORIDE SOLUTION

The invention relates to a method for the removal of metal impurities in a chloride-based copper recovery process. According to this method, the amount of metal impurities in a strong chloride solution of monovalent copper can be reduced to very low levels by using ion exchange as at least one purification stage, especially chelating ion-exchange resins.

US patent publication 6,007,600 describes a method for the hydrometallurgical production of copper from copper-containing raw materials such as copper sulphide concentrate. According to the method the raw material is leached counter-currently with a strong sodium chloride-copper chloride solution in several stages to form a monovalent copper(I) chloride solution. Since both some divalent copper chloride and impurities composed of other metals always remain in the solution, reduction of the divalent copper and solution purification are performed. The pure cuprous chloride solution is precipitated with sodium hydroxide to copper oxidule (cuprous oxide) and the oxidule is reduced further to elemental copper. The sodium chloride solution generated during copper oxidule precipitation is treated further in chlorine-alkali electrolysis, and the chlorine gas and/or chloride solution obtained from this is used in raw material leaching, the sodium hydroxide formed in electrolysis for oxidule precipitation and the forming hydrogen for the reduction of copper to elemental copper. US patent publication 6,007,600 focuses on the copper recovery method as a whole, but solution purification for example is not described in detail.

US patent publication 5,487,819 also describes a method for the hydrometallurgical production of copper from a copper-containing raw material such as copper sulphide concentrate. According to the method, the raw material is leached counter-currently with a sodium chloride-copper chloride solution in several stages in order to form a monovalent copper(I) chloride solution. The solution generated is subjected to ordinary solution

purification as hydroxide precipitation, described in example 6. Zinc and lead contents in the cuprous chloride solution after solution purification are at a level of 2 – 3 g/l, and the solution is fed to copper electrolysis.

- 5 When one wishes to reduce the impurity level of a copper chloride solution as much as possible, for instance down to a few mg/l or less, ordinary hydroxide precipitation is not sufficient to reach this level, without a great deal of copper being precipitated together with impurities. It is of course clear that it is worth precipitating the majority of metal impurities by normal
10 methods, but the final purification has been problematic, since for instance the permitted impurity content of LME-A level cathode copper is rather small (BS 6017:1981).

15 In the types of processes described above the original material i.e. copper concentrate is leached into a strong alkali chloride solution, containing for example at least 200 g/l NaCl or other alkali chloride. Copper and metal impurities are then present in the solution as chloride complexes, usually with a negative charge. Copper is mainly present in the solution in mono-valent form.

20 In their article: "Ultra high purification of copper chloride solutions by anion exchange", Hydrometallurgy 45 (1997), pp. 345-361, Kekesi, T. and Isshiki, M. suggested anion-exchange resins for the purification of a copper chloride solution. The disadvantage is however, that it requires a large quantity of
25 resin, multi-stage washing to remove metal impurities from the resin, and a separate stage for the separation of lead for example.

Chelating ion exchangers have been researched for the removal of base metals such as zinc, cadmium, copper and nickel from metal plating
30 solutions. One study is described in the article by Koivula, R. et al: "Purification of metal plating rinse waters with chelating ion exchangers",

Hydrometallurgy 56 (2000) pp. 93-108. The chloride contents of the solutions were however in the range of some milligrams per litre.

US patent publication 4,895,905 describes a method for the removal of alkali earth or heavy metals from a strong NaCl solution using chelating resins. The amount of alkali earth and heavy metals before resin treatment was at the most about one hundred mg/l and after treatment the majority of metals were undetectable. The patent concentrates largely on resins where the functional group is alkylaminophosphonic.

The method of the invention relates to the removal of metal impurities from a strong chloride solution of monovalent copper to the level where the amount of metal impurities is only a few milligrams per litre. The removal of metal impurities is implemented at least partly using ion exchange, in particular with chelating ion-exchange resins. The term strong chloride solution refers to a solution where the amount of alkali chloride such as sodium chloride is at least 200 g/l. The amount of copper, especially monovalent copper, in the solution is in the order of 30 – 100 g/l. Particularly in processes where the final product, metallic copper, is formed by precipitation, the amount of metal impurities should be reduced in the solution from which the precipitation is to occur, since the impurities will be precipitated alongside the copper in the precipitation stage.

The essential features of the invention will be made apparent in the attached claims.

If divalent copper is present in the monovalent copper chloride solution, it is first removed by some appropriate method. The principal metal impurities in copper concentrate are zinc, lead, nickel, iron and manganese, and they appear in a chloride solution in divalent or trivalent form. The majority of unwanted divalent metals can most advantageously be removed using conventional precipitation methods such as hydroxide precipitation.

Precipitation can however be carried out in connection with the method according to the present invention so that 0.1 – 1 g/l of metal impurities are left in the solution. This avoids the precipitation of copper along with other metals, which would cause fruitless recirculation and copper losses.

5

The removal of metal impurities from a copper chloride solution down to a level of a few milligrams is performed using a chelating ion-exchange resin. The functional group of ion-exchange resin is preferably the iminodiacetic acid group or the aminophosphonic group ($-\text{CH}_2\text{-NH-CH}_2\text{-PO}_3\text{Na}_2$). The property they have in common is a styrene-divinyl-benzene matrix of ring structure and a certain functional group that is selective for certain metals. A divalent or trivalent metal, such as zinc, lead, nickel, iron and manganese, can be bound to the functional group in place of the sodium. Since the resin does not bind monovalent copper so strongly, it remains in the chloride solution and passes through the resin. The metals bound to the resin are eluted with hydrochloric acid and the solution obtained is returned to the process so that the metal impurities are finally removed from the process via the precipitation stage.

20 Since the resin used binds divalent copper about as strongly as it binds the metal impurities, the oxidizing effect of the air must be eliminated so that the monovalent copper is not oxidized into divalent.

The dissolution of monovalent copper into water is based on chloride complexes so that the solution is stable only in a strong chloride solution, an acidic or neutral environment. Therefore the process solution that is the mother liquor in the resin (monovalent copper chloride solution) has to be displaced with an NaCl solution before elution, and correspondingly before the process solution is fed into the resin after regeneration, the equipment that contains resin must be filled with an NaCl solution instead of the alkaline regeneration solution.

30

We have found that by using the above ion-exchange resin for the purification of monovalent copper chloride solution it is possible to achieve an impurity level in the solution that corresponds to cathode copper grade LME-A or even purer.

5

The method is described further by the following examples.

Example1

Tests were carried out in 50 ml burettes. The feed rate of the solution through the column was 300 ml/h. Samples of the outflowing solution were taken every hour. After the test 150 ml of NaCl solution was fed through the column, after which the column was eluted with a 10 % HCl solution for three hours at a rate of 100 ml/h. During elution 5 samples were taken. After elution 150 ml of water was fed through the column and finally the resin was regenerated by feeding 300 ml of NaOH solution (NaOH = 80 g/l) through the column.

The solution for purification contained about 200 mg/l of lead and zinc, and about 50 mg/l of iron, manganese and nickel, and its pH was 6. The same solution was fed to each of the three columns with separate hose pumps.

Three resins were used in the tests in parallel columns. A summary of their basic characteristics is shown in Table 1.

Table 1. Properties of ion-exchange resins used in tests

Resin	I	II	III
Matrix	Styrene divinylbenzene	Styrene divinylbenzene	Styrene divinylbenzene
Functional group	Iminodiacetic	-CH ₂ -NH-CH ₂ -PO ₃ Na ₂	Iminodiacetic
Ion form	Na ⁺	Na ⁺	Na ⁺
Capacity, eq/l	≥ 1.25	≥ 1.0	≥ 1.0

5 Table 2. Ion-exchange test results

TEST	SAMPLE	TIME h/min	Cu g/L	Zn mg/L	Pb mg/L	Fe mg/L	Mn mg/L	Ni mg/L
Resin I	Charging	Feed solution	52.8	203	140	49.0	37.8	36.6
	Charging	1 h	52.0	<0.5	<1	2.9	<0.25	<0.5
	Charging	2 h	53.9	<0.5	<1	3.1	0.51	<0.5
	Charging	3 h	53.5	0.66	23.0	4.7	3.5	<0.5
	Brine rinse	Composite sample	11.0	63.9	146	1.6	16.2	1.7
	Elution	15 min	0.447	907	124	416	1012	943
	Elution	30 min	0.516	3 355	1 466	209	132	227
	Elution	1 h	0.124	1 195	1 010	0.86	0.38	2.2
	Elution	2 h	0.035	352	69	0.34	<0.1	0.35
	Elution	3 h	0.010	166	2.4	0.39	<0.1	0.37
	Water rinse	Composite sample	0.003	144	<1	0.45	<0.1	<0.2
	Regeneration	Composite sample	0.001	1.4	<1	0.30	<0.1	<0.2
Resin II	Charging	Feed sample	52.8	203	140	49.0	37.8	36.6
	Charging	1 h	52.6	<0.5	<1	1.4	<0.25	<0.5
	Charging	2 h	51.5	<0.5	<1	7.6	<0.25	<0.5
	Charging	3 h	53.3	<0.5	5.2	4.0	0.45	<0.5
	Brine rinse	Composite sample	11.4	36.7	70.6	1.1	5.1	3.8
	Elution	15 min	1.06	4 130	570	11.4	2 120	3 610
	Elution	30 min	0.242	2 850	1 490	102	118	4.1
	Elution	1 h	0.064	465	1 500	17.8	<0.1	<0.2
	Elution	2 h	0.009	68.5	950	6.9	<0.1	<0.2
	Elution	3 h	0.002	11.1	1.6	1.2	<0.1	<0.2
	Water rinse	Composite sample	0.024	7.4	<1	0.44	<0.1	0.28
	Regeneration	Composite sample	0.002	2.5	<1	3.0	<0.1	<0.2
Resin III	Charging	Feed sample	52.8	203	140	49.0	37.8	36.6
	Charging	1 h	35.3	<0.5	<1	1.2	0.25	<0.5
	Charging	2 h	53.0	<0.5	5.5	3.7	1.1	<0.5
	Charging	3 h	54.7	<0.5	35.7	2.9	6.7	<0.5
	Brine rinse	Composite sample	13.1	31.0	45.8	1.6	7.7	0.7
	Elution	15 min	0.813	410	73.3	383	778	764
	Elution	30 min	0.931	2 395	1 620	133	135	165
	Elution	1 h	0.457	986	975	1.0	0.33	1.1
	Elution	2 h	0.190	379	111	0.51	<0.1	<0.2
	Elution	3 h	0.076	190	9.5	0.77	<0.1	<0.2
	Water rinse	Composite sample	0.019	360	3.4	0.25	<0.1	<0.2
	Regeneration	Composite sample	0.010	4.7	<1	0.40	<0.1	<0.2

Table 2 shows that all the selected resins were able to remove the impurities required. Resin II performed best, being able to produce a solution of the

required purity in over two hours. The selected resins acted far better in a copper(I) chloride-sodium chloride solution than other resins that were tried, which were unable to perform selectively as desired.

5 Example 2

A pilot test was carried out in glass columns with an outer diameter of 70 mm (wall thickness 4.2 mm) and a height of 1000 mm (straight section). The total volume of the column was 3 litres and 2 litres of resins were then added. The resin used in the pilot was resin II. There were two columns in
10 series in the run and the flow occurred from the top to the bottom without intermediate pumping. In front of the columns there was a column filled with copper chips, with the purpose of reducing the copper that had oxidized during intermediate storage to monovalent copper.

15 At first both columns were changed once every 24 hours and eluted. Later only the first of the columns was subjected to elution, the second column was used as the first and the ready eluted column was used as the final column. The elution frequency was changed so that it depended on the amount of impurities in the feed solution, generally every 2 - 3 days.

20 In the first test campaign the concentrate used contained very little nickel and manganese and thus their amount in the ion-exchange feed solution was below the analysis limit. The zinc content in the feed solution varied between 100 – 900 mg/l with an average of 340 mg/l. The lead content varied
25 between 3 – 70 mg/l with an average of 21 mg/l. In the product solution 80 % of the zinc analyses were below the analysis limit (0.5 mg/l) as were 58 % of the lead analyses (analysis limit 1 mg/l). In the analyses of the copper product reduced from copper oxidule zinc was typically below 1 ppm and lead below 0.5 ppm.

30 In the second test campaign a concentrate was used with a lead content of about twice that of the concentrate used in the first campaign. The contents

of the impurities relevant with regard to ion exchange did not differ greatly from those of the previous campaign.

5 The zinc content of the feed solution varied in this campaign between 120 - 920 mg/l with an average of 390 mg/l. The lead content at the start of the series was 75 mg/l, rising to a level of 440 mg/l at the end of the series. Nickel was again below the analysis limit of 0.5 mg/l, and the manganese content was between 0.1 - 1.2 mg/l.

10 95 % of the product solution zinc analyses were below the analysis limit (0.5 mg/l) as were 42 % of the lead analyses (analysis limit 1 mg/l). The nickel and manganese contents were again very low.

In the analyses of the copper product reduced from copper oxidule zinc was on average 1.3 ppm and lead 0.55 ppm i.e. the copper product was of LME-
15 A quality.

PATENT CLAIMS

1. A method for the removal of metal impurities in chloride-based copper recovery processes, **characterised in that** the metal impurities are removed from a strong chloride solution of monovalent copper using ion exchange.
2. A method according to claim 1, **characterised in that** chelating ion-exchange resins are used for the removal of metal impurities.
3. A method according to claims 1 or 2, **characterised in that** there is a styrene-divinyl-benzene matrix of ring structure in the ion-exchange resin.
4. A method according to some of the above claims, **characterised in that** the functional group of the ion-exchange resin is the iminodiacetic acid group.
5. A method according to claims 1, 2 or 3, **characterised in that**, the functional group of the ion-exchange resin is the aminophosphonic group.
6. A method according to some of the above claims, **characterised in that** the metal impurity to be removed is one or more of the group of zinc, nickel, lead, iron and manganese.
7. A method according to some of the above claims, **characterised in that** the alkali chloride content of the strong chloride solution is at least 200 g/l.

8. A method according to some of the above claims, **characterised in that** the amount of monovalent copper in the solution to be purified is 30 – 100 g/l.
- 5 9. A method according to some of the above claims, **characterised in that** the removal of metal impurities is carried out in an acidic environment.
- 10 10. A method according to some of the above claims, **characterised in that** the removal of metal impurities is carried out in a neutral environment.
- 15 11. A method according to some of the above claims, **characterised in that** the copper-containing chloride solution that is the mother liquor in the resin is displaced before elution with an NaCl solution and that the alkaline solution to be used for regenerating the resin is displaced with an NaCl solution before the copper-containing chloride solution is fed into the resin.
- 20 12. A method for the removal of metal impurities in chloride-based copper recovery processes, **characterised in that** the majority of the metal impurities in the strong chloride solution of monovalent copper are removed by hydroxide precipitation and the rest by using ion exchange.
- 25 13. A method according to claim 10, **characterised in that** the metal impurities are removed by hydroxide precipitation to a content of 0.1 – 1 g/l, after which the final purification is made using ion exchange.
- 30 14. A method according to some of the above claims, **characterised in that** impurities are removed from a strong chloride solution of copper

by ion exchange at least to a level that corresponds to cathode copper LME-A grade impurity level.

- 5 15. A method for the counter-current leaching of copper raw material with a strong sodium chloride-copper chloride solution in several stages in order to form a monovalent copper(I) chloride solution and to purify the solution, which said cuprous chloride solution is precipitated as copper oxidule using alkali hydroxide and the oxidule is reduced further to elemental copper, and the sodium chloride solution forming
10 in connection with copper oxidule precipitation is processed further in chlorine-alkali electrolysis, **characterised in that** purification of monovalent copper(I) chloride solution from metal impurities is carried out at least partially using ion exchange.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 03/00292

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22B 3/42 // C22B 15:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	METALLURGICAL AND MATERIALS TRANSACTIONS B, Volume 28B, No 987, December 1997, Tamas Kekesi et al, "Preparation of Ultra-High-Purity Copper by Anion Exchange" --	1,6,9-10
X	US 3951649 A (OLMEDO KIESWETTER, JR. ET AL), 20 April 1976 (20.04.76), column 2, line 58 - line 63; column 5, line 41 - line 56 --	1,6
A	US 4297183 A (ANDRE GEORGEAUX), 27 October 1981 (27.10.81), claims 1-2, abstract --	1-15

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 July 2003

Date of mailing of the international search report

04-07-2003

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Mårten Hulthén/MP

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 03/00292

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3873668 A (LESTER RUSSELL), 25 March 1975 (25.03.75), column 6, line 31 - line 35, abstract --	1-15
A	US 6007600 A (OLLI HYVÄRINEN ET AL), 28 December 1999 (28.12.99) --	1-15
A	HYDROMETALLURGY, Volume 56, 2000, Risto Koivula et al, "Purification of metal plating rinse waters with chelating ion exchangers" page 107 -- -----	5

INTERNATIONAL SEARCH REPORT
Information on patent family members

02/06/03

International application No.

PCT/FI 03/00292

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
US	3951649	A	20/04/76	NONE	
US	4297183	A	27/10/81	AT 1831 T	15/12/82
				AU 538721 B	23/08/84
				AU 6156280 A	04/03/82
				BR 8005329 A	04/03/81
				CA 1156471 A	08/11/83
				DE 3061108 D	00/00/00
				DK 148284 B,C	28/05/85
				DK 362080 A	25/02/81
				EP 0024987 A,B	11/03/81
				SE 0024987 T3	
				ES 494351 A	01/08/81
				ES 8106241 A	16/10/81
				FI 66921 B,C	31/08/84
				FI 802623 A	25/02/81
				FR 2463639 A,B	27/02/81
				GR 69806 A	12/07/82
				IE 50094 B	05/02/86
				IE 801688 L	24/02/81
				JP 56038437 A	13/04/81
				JP 63049732 B	05/10/88
				MX 153805 A	31/12/86
				NO 154748 B,C	08/09/86
				NO 802512 A	25/02/81
				PL 123202 B	30/09/82
				PL 226367 A	22/05/81
				PT 71719 A,B	01/09/80
				ZA 8005160 A	30/09/81
US	3873668	A	25/03/75	NONE	
US	6007600	A	28/12/99	AU 738376 B	13/09/01
				AU 8187698 A	11/03/99
				CA 2246089 A	28/02/99
				FI 104837 B	00/00/00
				FI 973566 A	01/03/99